The Absorption of Light by Elements in a State of Vapour : The Halogens.

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[PLATE 7.]

In previous papers* we have given an account of the effect produced on the light of the Nernst filament by passing it through the vapour of the elements of the sulphur, phosphorus and mercury groups and have shown the bearing of the phenomena observed upon the constitution of the vapour in each case. In the present paper we propose to deal with chlorine, bromine, and iodine, the only other elements which lend themselves readily to this method of investigation.

Ten years ago the absorption spectra of bromine and iodine were investigated by Evans† by a method similar to that which we employ. He showed that the absorption varies with the temperature and pressure and drew from his results the conclusion that at sufficiently high temperatures the vapour of these elements is diactinic. This he explained by assuming that the monatomic molecules into which the more complex molecules are gradually resolved as the temperature is raised are colourless and without absorbent action on light at any rate within the limits $\lambda\,3500$ to $\lambda\,6800$. In most of his experiments the pressure was kept constant by connecting the observation tube in which the vapour was heated with a reservoir of the element maintained at a constant and lower temperature. The mass of the vapour at different temperatures was, therefore, variable. Our experiments were designed to show the effect produced by a constant mass of vapour on the absorption when the temperature was varied over as wide a range as possible. For this purpose a known quantity of the element under examination was enclosed in a sealed vacuous tube and the temperature gradually raised, observations upon the absorption being made at intervals. Under these conditions while the mass of the vapour remains the same throughout, the pressure increases both with the rise of temperature and as a consequence of the dissociation of the molecules. As, however, the tubes were evacuated with the Sprengel pump and the initial pressures were, therefore, low, it is improbable that the changes of pressure had any great influence upon the phenomena. This view is confirmed by the fact that observations

made upon different quantities of the element showed only such differences of spectra as might be expected from the variation in the mass of the substance employed. In no case, so far as we observed, was the temperature of maximum absorption altered.

In our experiments on bromine, quantities varying from 1·4 mgrm. to 17 mgrm. were employed. The bromine was introduced into the observation tube by weighing a quantity of the dried double bromide of gold and potassium in a small capillary tube and placing this in the side tube* of the observation apparatus, evacuating, and sealing. The double bromide was then decomposed by heating, and the side tube sealed off at a point between the capillary tube and the body of the apparatus thus leaving bromine alone in the apparatus. By this means we were able without difficulty to get any required quantity of pure bromine into the tube. The quantity of bromine was checked by titration after each experiment. The observation tubes were of the same dimensions as those employed in the previous investigations (*loc. cit.*).

When the light from a Nernst filament is allowed to fall upon a white screen after passing through the vapour of bromine, a remarkable series of changes is observed as the temperature is raised. At 100° C. the colour, which is deep orange at lower temperatures, changes to brick red; above 600° C. the intensity of the transmitted light diminishes, the effect being most pronounced at 900° C. when the vapour is almost opaque. Above this point the brick-red colour changes to orange red; at 1200° C. it is pale yellow and at still higher temperatures nearly white.† In this connection it is interesting to recall that Andrews pointed out long ago‡ that when bromine is heated in a sealed tube it gradually becomes quite opaque.

Fig. 1 shows the absorption spectra of 9·7 mgrm. of bromine between the temperatures of 22° C. and 1350° C. It will be noticed that the absorption increases regularly up to about 900° C. after which it falls off continuously. The results are similar when larger quantities of bromine are employed (fig. 2), the absorption being of course greater, but the curve remaining of the same general form with the point of maximum absorption at the same temperature.

With 3 mgrm. of bromine a wide absorption band makes its appearance, the middle of which is situated about λ 4170. This band dies out about 600° C. but the spectrum remains weak in the same region until a much higher

* See fig. 1, ' Roy. Soc. Proc.,' A, vol. 95, p. 484 (1919).

† These observations were made on quantities of 8 or 9 mgrm. of bromine in observation tubes, 100 mm. long, 12·5 mm. diameter. When a larger quantity of bromine was employed, the light transmitted at 900° C. was so feeble that it could hardly be observed on the screen.

‡ ' Report Brit. Assoc., Edinb.,' 1871.

temperature is reached. Evans found in his experiments that there was no absorption at 1320° C., the highest temperature he employed. It seems possible, having regard to his method of observation, that what really happened was that the quantity of vapour remaining in his tube at the higher temperatures was too small to show any absorptive effect. In any case, his explanation that the disappearance of the absorption was due to the resolution of the diatomic into colourless monatomic molecules can hardly be correct seeing that at the highest temperature he reached it is probable that half the molecules remain undissociated.

Iodine vapour, like that of bromine, changes colour as the temperature is raised. It was observed that with 4 mgrm., the colour which was reddish violet up to about 300° C. gradually deepened in shade to about 500° C. At this temperature the intensity of the transmitted light was greatly diminished and remained feeble up to about 800° C. when it again increased, the violet shade becoming lighter. At still higher temperatures the violet passed gradually into a bright salmon colour and finally the colour disappeared almost entirely.

The general character of the spectrum* is the same as in the case of bromine, but the point of maximum absorption, about 600° C., is much lower and the wide absorption band is much more distinctly defined. It will be remembered that the temperature of maximum absorption of tellurium is much higher than that of sulphur or selenium, the elements of lower atomic weight in the same group. With the halogens the reverse is the case. Figs. 3 and 4 show the absorption obtained with 2·8 and 4 mgrm. of iodine respectively. Fig. 4 shows a series of faint bands extending from λ 3990 to λ 4420 which first show distinctly at a temperature of 900° C. As the iodine was specially purified these bands must be due to the element and not to some foreign substance.

To obtain the spectrum shown in fig. 4 the temperature was raised to 1350° C., the highest point possible with silica tubes. It is interesting to observe that even at this temperature the wide band has not entirely died out, and the faint bands between λ 3990 and λ 4420 are still observable.† We are therefore unable to confirm Evans' statement as to the disappearance of the absorption spectrum at high temperatures. This is not surprising seeing that he examined the spectra by the eye. Without the aid of photography the faint lines would easily escape notice.

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* Wood ('Phil. Mag.,' 1912, p. 680, and 1918, p. 236) has shown that the iodine absorption spectrum has about 50,000 bands in the visible.

† Spectrum in fig. 4 was taken with a plate more sensitive to the red than that employed in photographing the other spectra.

The investigation of chlorine presents peculiar difficulties. A large quantity of the element, involving the use of a long tube, must be employed to give a mass of the gas sufficient to exhibit the absorption phenomena. The spectrum shown in fig. 5 was obtained with a tube 43 cm. long containing chlorine at a pressure of 0·72 atmosphere at 0° C. It will be seen that there is a gradual increase in the amount of absorption with the rise of temperature, but at 1190° C., the highest temperature we reached in this case, no reversal such as is exhibited by bromine and iodine is apparent. Whether or not reversal would take place at a still higher temperature it is impossible to say with certainty. It may, however, be pointed out that the narrow bands at the red end of the spectrum have become much sharper at the highest temperature reached. Similar behaviour is observed in all those elements where the absorption is reversed, when the temperature of maximum absorption is being approached. The spectrum, which had been examined by Mrs. Laird to ascertain the effect of pressure at room temperature[*] is of the same fluted character as the spectra of bromine and iodine. At the higher temperatures faint diffuse bands are found in the region λ 5450 to λ 6180.

The vapour densities of the halogen elements show remarkable abnormalities. At low temperatures they are all somewhat higher than is required by the diatomic molecule. Thus, according to Treadwell and Christie,[†] the molecular weight of chlorine at 20° C. is 72. Pier,[‡] states that chlorine does not obey the ordinary gas laws below 184° C., but that between 300° C. and 1450° C. it is normal. According to Langer and V. Meyer,[§] the density of chlorine begins to fall off above 1200° C., the diminution being due to the breaking up of the diatomic molecules.

Jahn[||] states that the density of bromine does not become normal till over 200° C.[¶] Perman and Atkinson[**] show that about 900° C. the vapour is dissociated to a small extent. According to Victor Meyer,[††] the density of iodine vapour at 253° C. is a little higher than corresponds with the formula I_2. The dissociation of diatomic iodine molecules takes place, according to all the observers, at a lower temperature than in the case of bromine, but marked dissociation appears to begin between 600° C. and

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[*] 'Astrophysical Journal,' vol. 14, p. 85 (1901).
[†] 'Zeit. für Angew. Chemie,' vol. 18, p. 1934 (1905).
[‡] 'Zeit. Physikal. Chem.,' vol. 62, p. 385 (1908).
[§] 'Ber.,' vol. 15, p. 2769 (1882).
[||] 'Gmelin Kraut,' vol. 1, sec. 2, p. 226.
[¶] See also Perman, 'Roy. Soc. Proc.,' vol. 48, p. 45 (1890).
[**] 'Roy. Soc. Proc.,' vol. 66, p. 10 (1899).
[††] 'Ber.,' vol. 13, p. 394 (1880).

700° C.; 50 per cent. of the molecules are probably dissociated about 1270° C.*

It will thus be seen that in the case of the halogens there is evidence from the density that some of the molecules at low temperatures contain more than two atoms, and that at high temperatures the diatomic are mixed with monatomic molecules. It is remarkable that the temperatures at which the vapour density of bromine and iodine is stated to show a distinct falling off from the normal are precisely the temperatures at which we find the absorption to be at its maximum. Thus, according to Meier and Crafts,† the density of iodine begins to fall off between 600° C. and 700° C., and this is the temperature of maximum absorption. Again, according to Perman,‡ at 900° C. marked dissociation of bromine vapour is first observed; this is also the temperature of maximum absorption.

The fact that the absorption increases with the temperature up to a certain point is probably connected, as in the case of sulphur, with the gradual breaking down of more complex into simpler molecules. The vapour densities of the halogen elements at low temperatures point to the existence of aggregates of greater complexity than diatomic. As the temperature is raised these gradually dissociate, until the vapour consists mainly, if not entirely, of diatomic molecules, some of which in turn break up into monatomic molecules. It may be supposed that during this last phase the nascent atoms of the halogen tend to combine with one another and with the undissociated diatomic molecules to form more complex and more highly absorptive molecules; in other words, that the element polymerises. Applying this view to iodine vapour, the number of such polymers of iodine is at a maximum somewhat above 600° C.

In considering the relation of absorption to the molecular condition of the vapour, it is to be remembered that the vapour density is an average value for all the molecular aggregates present in the vapour at the temperature at which the density is taken. A constant value may occur for the density over a wide range of temperature while the absorption varies considerably, if we assume, for example, in the case of the halogens, that a sufficient number of molecules greater than X_2 are present to balance the diminution of density caused by the dissociation of X_2 to 2X. Thus, with iodine there is a range of several hundred degrees over which the density appears to remain constant while the absorption shows a marked increase. The spectroscopic method, therefore, indicates a change

* Naumann, 'Ber.,' vol. 13, p. 1050 (1880).

† 'Ber.,' vol. 13, p. 851 (1880).
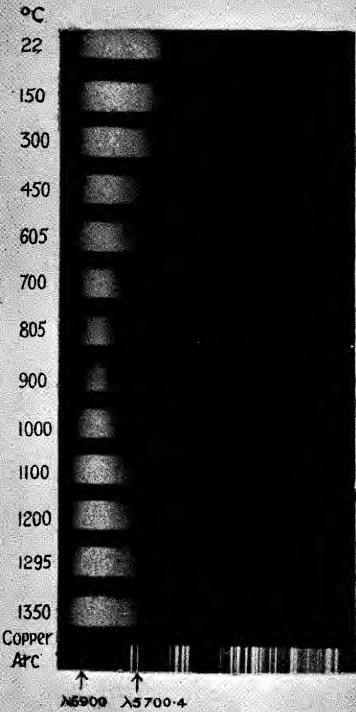
‡ 'Roy. Soc. Proc.,' vol. 66, pp. 17, 489 (1900).
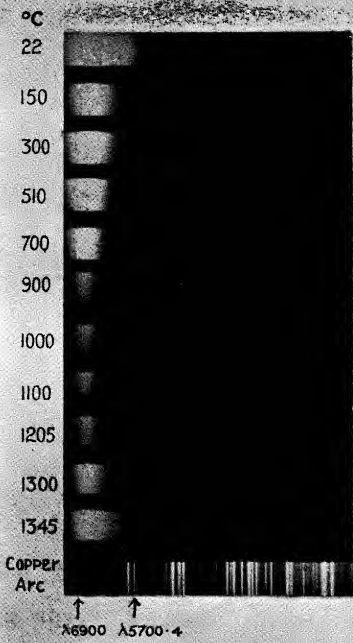
Fig. 1.-Spectrum of 9·7 mgm of Bromine

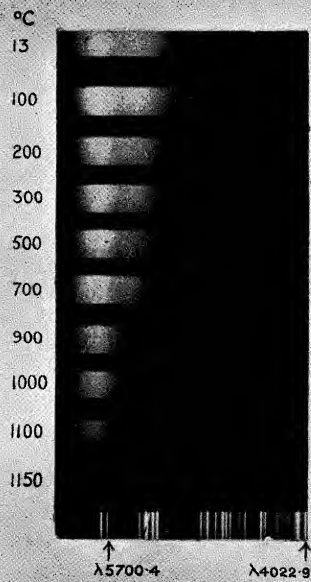Fig. 2.-Spectrum of 16·3 mgrm of Bromine

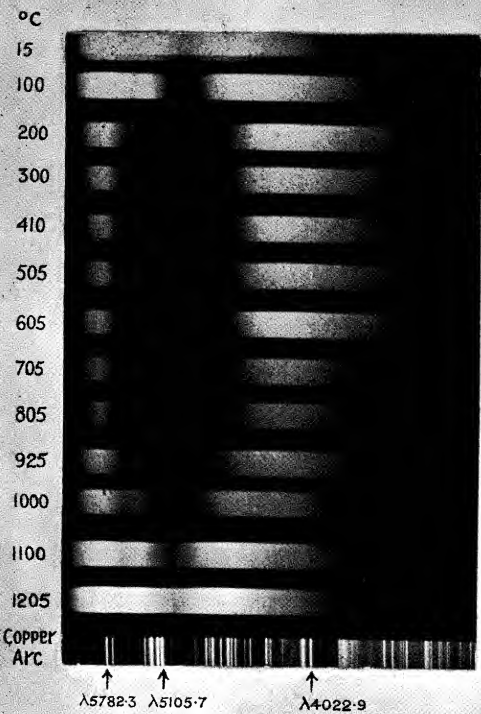Fig 5.-Spectrum of Chlorine at 0·72 atmosphere initial pressure
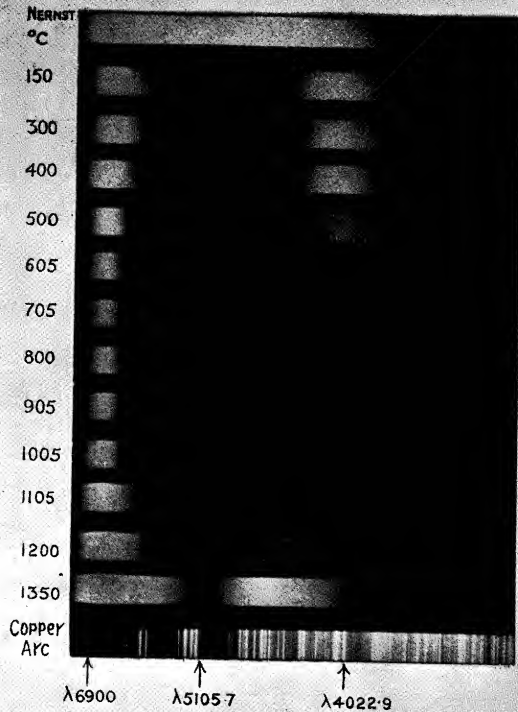
Fig 3.-Spectrum of 2·8 mgm of Iodine

Fig 4.-Spectrum of 4·0 mgm of Iodine

in the constitution of the vapour upon which the density throws no light.

As in the case of sulphur, it is equally impossible to explain the changes in absorptive power of the halogens on the hypothesis that the diatomic molecules are gradually broken down into monatomic molecules, and that no other change takes place. This would leave the change which occurs at the temperature of maximum absorption unexplained. Wood and Kimura had already come to the conclusion on other grounds that the change is not so simple as is generally assumed. They point out* that, " on the assumption that diatomic absorbing iodine breaks down into a colourless monatomic gas we should expect the spectrum to fade away precisely as it does when the amount of vapour is decreased by lowering the density." By comparing the absorption exercised by a bulb containing iodine at high temperature (about 1000° C.) and at a temperature of 35° C. they found that some of the lines were much stronger in the spectrum of the cold vapour than in the spectrum of the hot vapour, while with others the reverse phenomenon was observed. They concluded that, inasmuch as the lines are affected in different degrees by an elevation of temperature, something more complicated takes place than the dissociation of diatomic into monatomic molecules.

The association of the temperature of maximum absorption with a tendency to polymerize is not only in accord with what is known as to the varying valencies of the halogens, but also brings the phenomena into line with those exhibited by sulphur which are almost certainly connected with the similar tendency of this element to undergo polymerisation.

* 'Astrophysical Journal,' vol. 46, p. 181 (1917).

PLATE 7.

The fine bands, though distinct on the negatives, are not clear in Plate 7, owing to the limitations of half-tone reproduction.
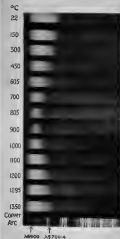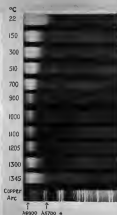
Fig.1.—Spectrum of 9·7 mgrm of Bromine

Fig.2.—Spectrum of 16·5 mgrm of Bromine

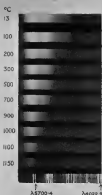Fig.5.—Spectrum of Chlorine at 0·72 atmosphere initial pressure
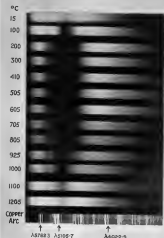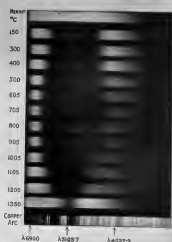
Fig.3.—Spectrum of 2·6 mgrm of Iodine

Fig.4.—Spectrum of 4·0 mgrm of Iodine

PLATE 7.

The fine bands, though distinct on the negatives, are not clear in Plate 7, owing to the limitations of half-tone reproduction.